

# The Influence of Chemical and Physical Forms of Ambient Air Acids on Airway Doses

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The effects of ambient relative humidity and particle size on acid deposition within the airways have been examined with a computer model. For  $\text{H}_2\text{SO}_4$  particles initially at 90% relative humidity in ambient air that are inhaled via the nose or mouth, there is significant deposition of acid in the airways even in the presence of typical values of respiratory  $\text{NH}_3$ . When these same particles are found in a fog at 100.015% relative humidity, there is significant deposition of acid in the nasal region during nose breathing but insignificant deposition to the deep lung for either nose or mouth breathing. The factors governing the partitioning of labile acid gases in the gas and liquid phases prior to inhalation are also discussed.

## Introduction

The relationship between acid particles in the atmosphere and human health has received considerable attention recently, as these proceedings attest. This paper will examine several aspects of human exposure, including the state of the acidic aerosol prior to inhalation and its subsequent fate within the respiratory tract up to the point of deposition to the airway surface.

## Atmospheric Exposure

The predominant particulate acid in the atmosphere is sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and its neutralization products with ammonia ( $\text{NH}_3$ ). The majority of the mass of acid found within these particles is contained within the accumulation mode at dry diameters ranging from 0.1 to 1.0  $\mu\text{m}$ . Changes in surrounding relative humidity (RH) can affect the size of the particles. At high RH, this effect can be dramatic. For instance, a  $\text{H}_2\text{SO}_4$  particle with a dry diameter of 1.0  $\mu\text{m}$  exists as a concentrated solution droplet at 90% RH with a diameter of approximately 2.5  $\mu\text{m}$ . At 99.4% RH, this same droplet exists at an equilibrium diameter of about 4.5  $\mu\text{m}$  and thus is approximately 100 times more dilute than the original dry  $\text{H}_2\text{SO}_4$  droplet. In a light fog at an RH of 100.015%, this droplet now has an

equilibrium diameter of approximately 30  $\mu\text{m}$  and is thus about  $3 \times 10^4$  times more dilute than the original dry droplet. The larger fog droplet also has a quite different deposition pattern upon inhalation than the same drop at a lower initial RH.

In addition, the relative amounts of labile acids dissolved within the particles can be quite different depending upon ambient RH. This relationship is summarized in Figure 1. The dissolved fraction of a given acid gas per cubic meter of air (mole in liquid phase/total mole) depends upon droplet pH and total condensed liquid water content. As shown in Figure 1, soluble gases such as nitric acid ( $\text{HNO}_3$ ) are found mainly in fog or cloud droplets but not in acid haze particles (pH < 2). In contrast, most sulfur dioxide ( $\text{SO}_2$ ) molecules are found in the gas phase for most atmospheric conditions. Not shown in Figure 1 are the organic acids, including hydroxymethanesulfonic acid, a strong acid formed from  $\text{SO}_2$  and formaldehyde. This latter acid is found only within dissolved droplets and exists at significant concentrations only in fogs (1).

Figure 1 can also be viewed with respect to respiratory uptake of various acid gases. Since  $\text{SO}_2$  is rapidly and efficiently removed in the upper airways, any gas equally diffusive and more soluble than  $\text{SO}_2$  will be removed at least as efficiently. Thus the acid gases in Figure 1 are expected to be removed in the extrathoracic region and upper airways when they are predominantly in the gas phase prior to inhalation. When they are found predominantly in the liquid

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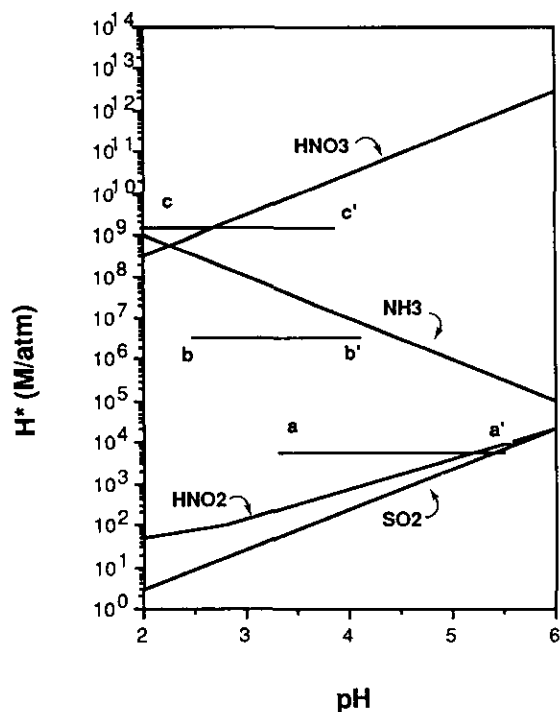


Figure 1. Summary of gas/liquid partitioning of selected acidic/basic species in the atmosphere. The ordinate is the effective solubility (Henry's) constant for a given species in units of mole/liter of water /atmosphere of gas, including the increased solubility of that species owing to dissociation in water. The abscissa is solution pH. The relationships for four atmospheric gases are given by the slanted lines at 20°C; solubility increases with increasing pH for the acid gases  $\text{SO}_2$ ,  $\text{HNO}_2$ , and  $\text{HNO}_3$ , and decreases for  $\text{NH}_3$ . The horizontal lines represent varying amounts of available liquid water typical of a dense cloud (aa'), a fog (bb'), and a humid haze (cc'). This plot is based on a similar one by Seinfeld (9).

phase in ambient air, their deposition pattern lies between two extremes, that of the pure gas as above and that of the particles themselves. The exact pattern depends upon the rate at which the gases are released from the droplets during airway passage. To assess the amount of acid deposition for various ambient aerosols, a lung deposition model was developed that includes the effects of particle size, breathing pattern, relative humidity and temperature (both ambient and airway) and respiratory ammonia concentrations.

## Airway Deposition Model

The description of particle deposition as a function of airway location is taken directly from Rudolf et al. (2,3). This empirical model views the respiratory tract as a series of filters, each with a unique efficiency for a given particle size that depends upon breathing pattern (volumetric flow rate and tidal volume) and upon particle physics (aerodynamic diameter and diffusivity). This model was modified to include the effect of hygroscopic growth (or shrinkage) of the particles as they experience varying relative humidity

(RH) values within the airways. As a particle changes size during passage through the respiratory tract, its deposition efficiency changes within a given region. Each of three regions (extrathoracic, tracheobronchial, and alveolar) were subdivided into 200 subsections in order to describe the chemical and physical state of particles traversing these regions and, therefore, better describe the overall deposition efficiency for a given particle within a given region. This new regional deposition efficiency (adjusted for changes in particle size within the airways) was estimated from the arithmetic mean value over all 200 sectors of  $(1 - d_i)$ , where  $d_i$  is the regional efficiency for a given particle size and breathing pattern (2,3). The model results are insensitive to arithmetic versus geometric mean descriptors but are dependent upon the RH profiles assumed to exist within the extrathoracic region (and trachea) during inhalation.

We report here results based upon a single set of assumed RH profiles patterned after those described by Martonen (4). The profiles differ depending upon route of entry and the value of ambient RH. To simplify matters, we consider only  $\text{H}_2\text{SO}_4$  inhaled either via the nose or mouth and do not consider oronasal breathing. We also consider only two ambient RH values: 90% RH, hereafter referred to as haze particles; and 100.015% RH, hereafter referred to as fog particles. When breathing haze via the nose, the RH linearly increases from its initial value of 90% to a value of 99.0% in the oropharynx, and then linearly from this point to a value of 99.4% in the tracheobronchial region. The temperature linearly increases from its ambient value to a value of 37°C in the oropharynx. For haze particles inhaled via the mouth, the RH remains constant at 90% in the mouth and oropharynx and then increases to a final value of 99.4% in the tracheobronchial region. The temperature linearly increases from its initial value to a value of 37°C in the tracheobronchial region. When breathing fog particles via nose or mouth, the RH remains constant within the airways at 99.4%, and the temperature patterns are the same as when breathing haze.

The exact size of a given  $\text{H}_2\text{SO}_4$  particle as it traverses the airways is determined primarily by the assumed RH profile within the airways. However, it may also depend upon the rate of growth (or shrinkage) of the particle as it experiences changes in the surrounding RH. Therefore, we have computed these growth rates using the expression of Fukuta and Walters (5). The rate depends upon the dry particle mass and composition, the actual wet particle size, and the surrounding RH. Growth rates for  $\text{H}_2\text{SO}_4$  and its ammonium salts are in good agreement with those predicted from the more elaborate calculation of Cocks and Fernando (6) under different RH profiles. The sizes predicted by our equilibrium model are also in good agreement with those reported by Tang and Munkelwitz (7). A comparison of the deposition estimated from different droplet growth assumptions is shown in Figures 2 and 3 for haze and fog particles, respectively, during

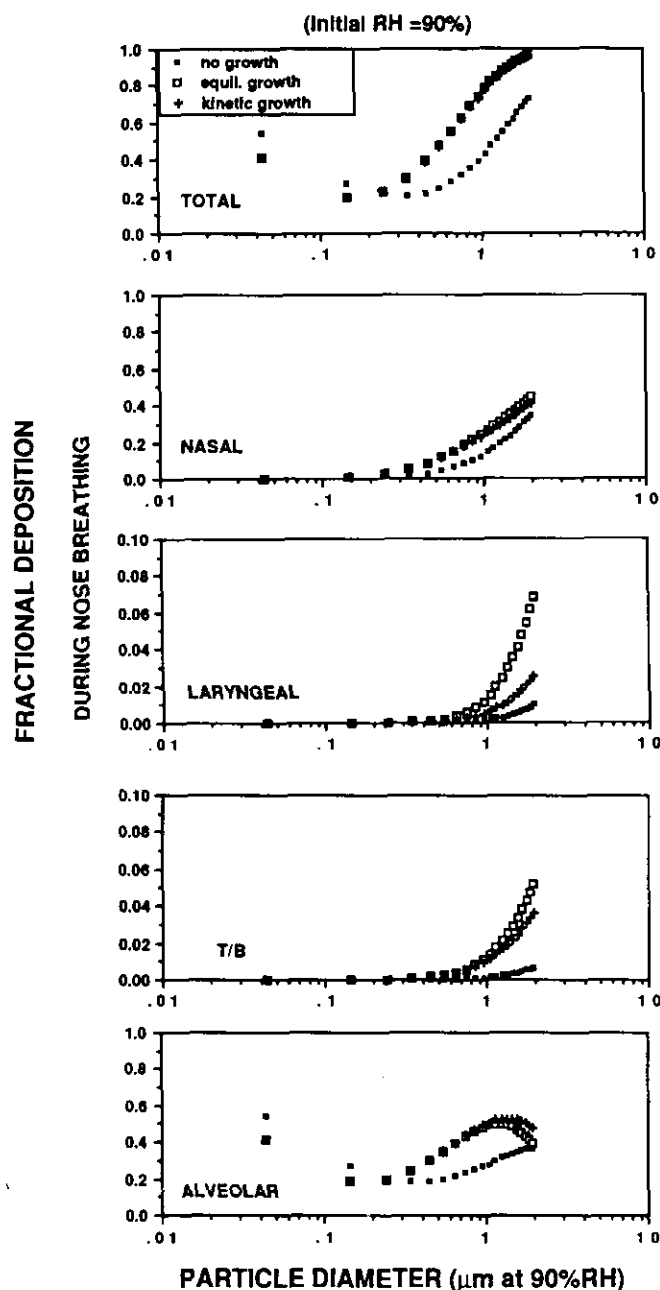


FIGURE 2. Calculated effect of hygroscopic growth of haze particles on their deposition in the human airways. The predictions were made using the compartmental model described by Rudolf et al. (2,3) modified to include droplet growth. The ordinate represents total deposited fraction during one breathing cycle. The abscissa is the actual geometric particle diameter at 90% RH prior to inhalation. The "no growth" case assumes that these aerosol droplets remain at their initial size at 90% RH throughout the breathing cycle; "equil. growth" assumes that particles grow fast enough to maintain their equilibrium size at all airway locations as RH increases during inhalation; "kinetic growth" allows the particles to grow at a rate specified by airway RH and particle size and thus the actual particle size may be less than the equilibrium size at a given airway location. The calculations are for nose breathing at 15 breaths/min.

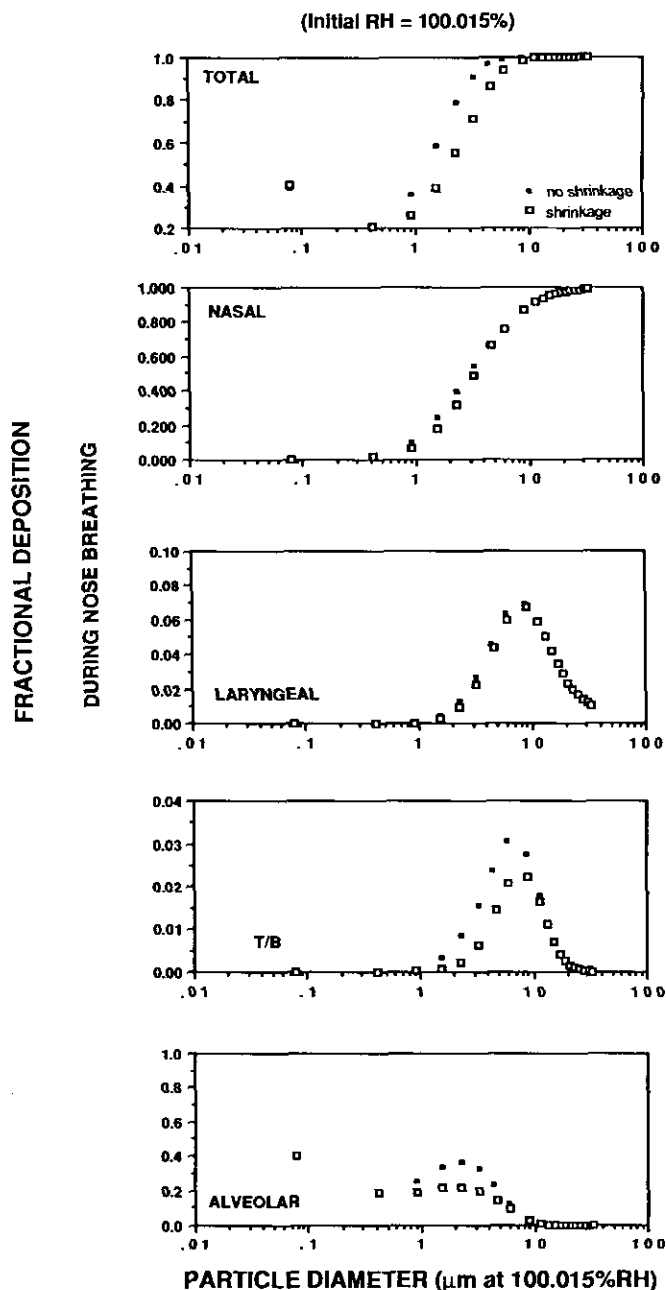


FIGURE 3. Calculated effect of hygroscopic shrinkage of haze particles on their deposition in the human airways. The predictions were made using the compartmental model described by Rudolf et al. (2,3) modified to include droplet shrinkage. The ordinate represents total deposited fraction during one breathing cycle. The abscissa is the actual geometric particle diameter at 100.015% RH prior to inhalation. The "no shrinkage" case assumes that these aerosol droplets remain at their initial size at 100.015% RH throughout the breathing cycle; "shrinkage" allows the particles to shrink at a rate specified by airway RH and particle size. In this calculation, airway RH is constant at 99.4%. The calculations are for nose breathing at 15 breaths/min.

nose breathing. As others have shown, the overall effect of hygroscopic growth within the airways is important. Although there is negligible difference between the explicit growth and the equilibrium growth models, there are subtle differences in the pattern of deposition.

To include the effect of chemical neutralization of inhaled acid particles by respiratory  $\text{NH}_3$ , we have employed the gas-phase diffusion limiting model of Larson et al. (8). Two different  $\text{NH}_3$  profiles were assumed, depending upon the route of entry. During inspiration via the nose, gaseous  $\text{NH}_3$  is 10 ppb in the nasal passages with a step change to 100 ppb in the oropharynx that decreases linearly and rapidly back to 10 ppb in the trachea. During inhalation via the mouth, the value increases linearly from 10 ppb at entry to 500 ppb at the oropharynx, decreasing rapidly again to 10 ppb within the trachea.

## Model Predictions

Figures 4 and 5 show the effect of both initial ambient RH (that is, initial particle size) and respiratory  $\text{NH}_3$ , on the deposition of acid for nose and mouth breathing, respectively. For ease of comparison, the deposition values are plotted against dry particle size where initially  $d_{\text{dry}} < d_{\text{haze}} < d_{\text{fog}}$ . During nose breathing, the fog particles are primarily deposited in the nasal region, whereas the haze particles are deposited in both the nasal and the alveolar regions. The smallest fog particles that penetrate the nose ( $d_{\text{dry}} < 0.3 \mu\text{m}$ ) are efficiently deposited in the alveolar region. Intermediate-size fog particles ( $0.3 < d_{\text{dry}} < 0.7 \mu\text{m}$ ) are deposited in both the laryngeal and tracheobronchial regions to a greater extent than haze particles of a similar dry size.

Respiratory  $\text{NH}_3$  lowers the acid deposition values in all cases. This is also shown in Figures 4 and 5. The larger fog particles are neutralized more rapidly because they have a larger surface-to-acid mass ratio than haze particles of a similar dry size. Notably, haze particles with  $d_{\text{dry}} < 0.3 \mu\text{m}$  are relatively unaffected by  $\text{NH}_3$  during nose breathing.

For inhalation via the mouth (Fig. 5), the smaller fog droplets ( $d_{\text{dry}} < 0.3 \mu\text{m}$ ) are deposited mainly in the alveolar region, whereas the intermediate-size drops are deposited primarily in the larynx and tracheobronchial region. Haze particles are mainly deposited in the alveolar region. Owing to the higher levels in the mouth than the nose, respiratory  $\text{NH}_3$  has a greater effect during mouth breathing. Figure 5 shows that for fog particles the predicted deposition of acid is sensitive to the respiratory flow rate. For these particles, deposition is significantly higher in the larynx than in more distal regions. Acid deposition via larger haze particles ( $d_{\text{dry}} < 0.5 \mu\text{m}$ ) is relatively unaffected by  $\text{NH}_3$ , whereas acid deposition via smaller haze particles ( $d_{\text{dry}} < 0.5 \mu\text{m}$ ) is affected by respiratory  $\text{NH}_3$  (especially alveolar deposition).

In the simplest case, the effect of  $\text{NH}_3$  can be scaled linearly with airway concentration for a given  $\text{NH}_3$  profile. RH effects are not linearly scaled, but should give results similar to these unless airway RH exceeds 100% for significant periods of time. This latter possibility seems unlikely.

These predictions of particle deposition would be incomplete without also considering the actual size distribution of atmospheric acid aerosol. In ambient air, much more of the acid mass per cubic meter of air is contained in the  $0.3\text{-}\mu\text{m}$  diameter particles (dry size) than in  $1.0\text{-}\mu\text{m}$  particles or  $0.1\text{-}\mu\text{m}$  particles. Therefore, the previous predictions need to be weighted by an appropriate atmospheric size distribution. The results of this atmospheric weighting for nose and mouth breathing are shown in Figures 6 and 7, respectively. During nose breathing, fog particles deliver more acid to the airways (mainly to the nose itself) than do haze particles. The presence of respiratory  $\text{NH}_3$  reduces this acid deposition somewhat, but does not eliminate it. During mouth breathing, fog particles are deposited to a greater extent than haze particles (mainly in the larynx), but respiratory  $\text{NH}_3$  eliminates the delivery of acid via these larger drops.

These acidic deposition estimates have not quantitatively included the effect of additional deposition due to labile acids. For soluble acid gases such as  $\text{HNO}_3$ , there will be increased deposition of acid to the lower airways when breathing fog droplets. However, in this case not much acid reaches these surfaces when appreciable amounts of respiratory  $\text{NH}_3$  is present. Thus, most of the  $\text{HNO}_3$  is expected to be deposited in the nose and upper tracheobronchial region when breathing either haze or fog. In the former case, the acid is inhaled and rapidly removed as a gas, whereas in the latter case it is efficiently removed in large droplets by the extrathoracic airways. There is also a possibility that  $\text{HNO}_3$  gas can react directly with respiratory  $\text{NH}_3$  in the gas phase, forming very small ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) particles. These particles could penetrate deeper into the lung but would not by definition be an efficient acid vector.

This discussion has also not considered the deposition of acids absorbed on and within the porous surfaces of small combustion aerosols. These small particles may contain acid in small pores that was formed under the high temperatures of combustion. This subsurface acid would certainly be more resistant to chemical attack by respiratory  $\text{NH}_3$  and therefore these particles are a potentially significant vector of acid to the lower airways.

## Conclusions

In summary, we have examined the consequences of changes in ambient relative humidity on the partitioning of volatile acidic species between the gas and liquid phases and estimated the ultimate fate of these atmospheric particles upon inhalation. Although fog

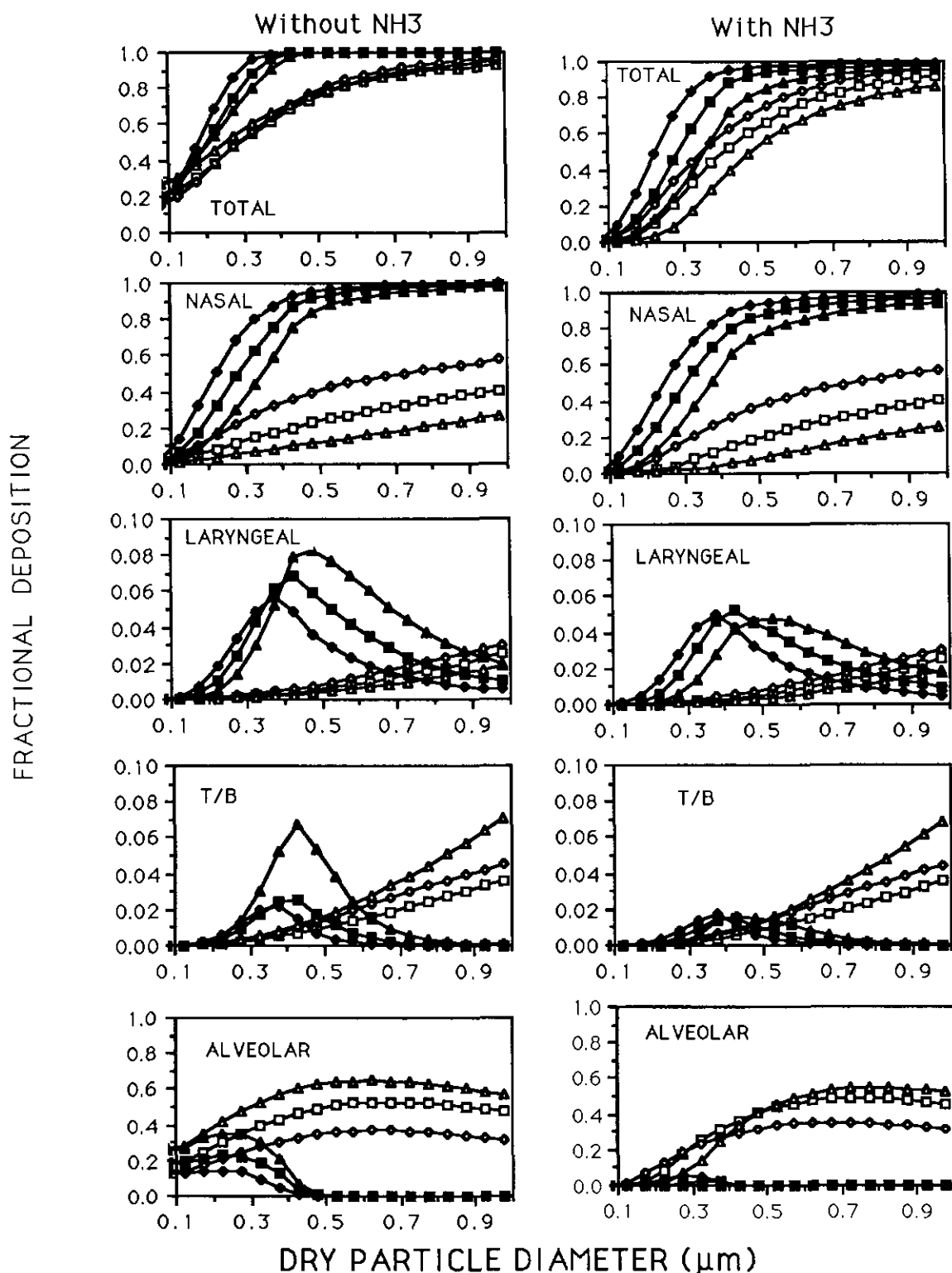


FIGURE 4. Estimated deposition of  $\text{H}_2\text{SO}_4$  particles during nose breathing as a function of dry geometric diameter, ambient RH, breathing pattern, and airway location. The calculations apply to one breathing cycle with and without the presence of respiratory  $\text{NH}_3$  (right and left panels, respectively). For a fixed tidal volume of 1 L, volumetric flow rate doubles from 125  $\text{cm}^3/\text{sec}$  ( $\blacktriangle$ ,  $\triangle$ ) to 250  $\text{cm}^3/\text{sec}$  ( $\blacksquare$ ,  $\square$ ), and again to 500  $\text{cm}^3/\text{sec}$  ( $\blacklozenge$ ,  $\lozenge$ ). Ambient RH represents humid haze at a value of 90% (open symbols) and fog at a value of 100.015% (filled symbols). These calculations include the effect of hygroscopic growth (or shrinkage) of particles in the airways.

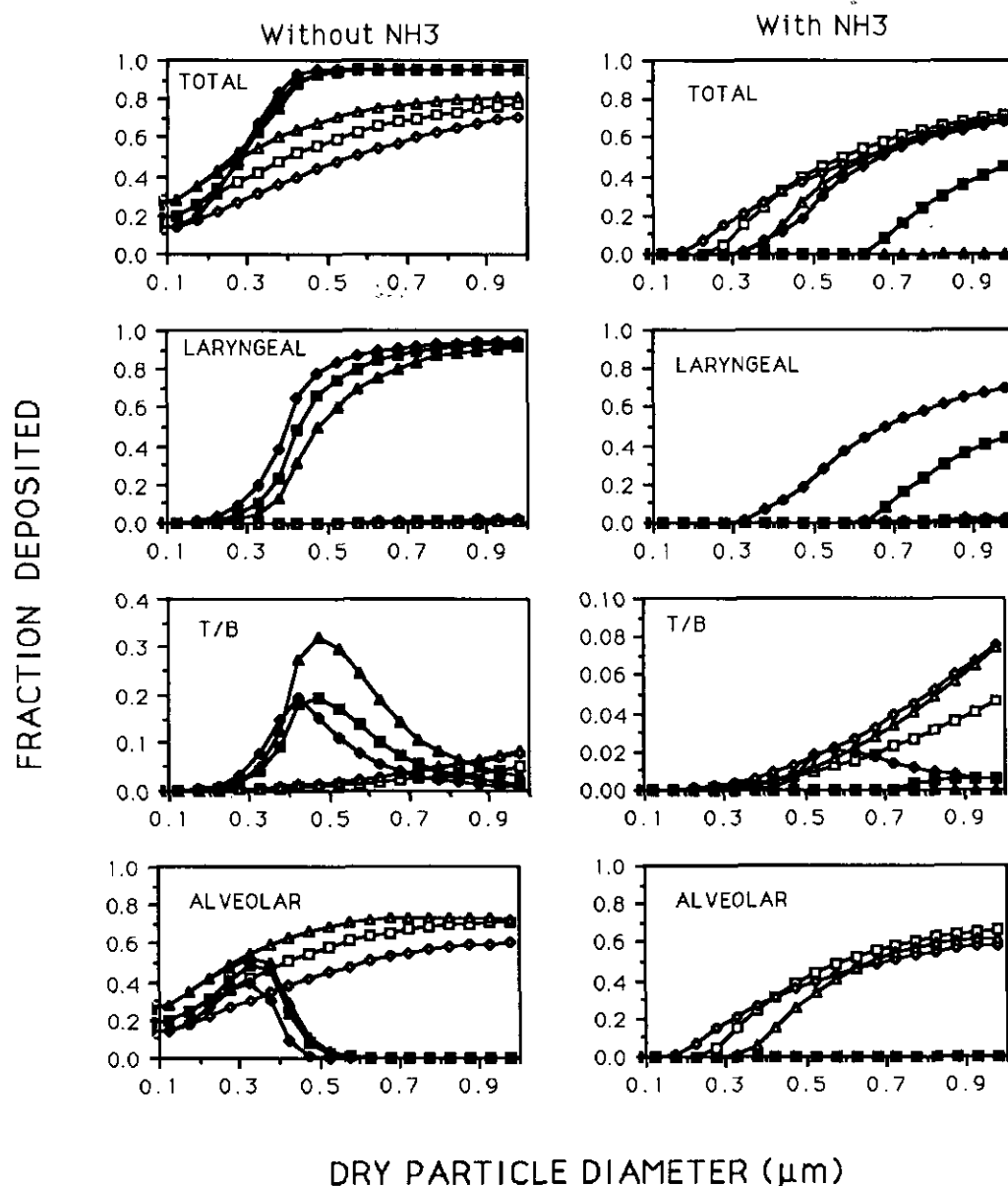


FIGURE 5. Estimated deposition of  $\text{H}_2\text{SO}_4$  particles during mouth breathing as a function of dry geometric diameter, ambient RH, breathing pattern, and airway location. The calculations apply to one breathing cycle with and without the presence of respiratory  $\text{NH}_3$  (right and left panels, respectively). For a fixed tidal volume of 1 L, volumetric flow rate doubles from 125  $\text{cm}^3/\text{sec}$  ( $\blacktriangle$ ,  $\triangle$ ) to 250  $\text{cm}^3/\text{sec}$  ( $\blacksquare$ ,  $\square$ ), and again to 500  $\text{cm}^3/\text{sec}$  ( $\blacklozenge$ ,  $\lozenge$ ). Ambient RH represents humid haze at a value of 90% (open symbols) and fog at a value of 100.015% (filled symbols). These calculations include the effect of hygroscopic growth (or shrinkage) of particles in the airways.

droplets can potentially sequester more acidic gases than smaller, subsaturated haze particles, the fog droplets are also susceptible to a greater extent of chemical neutralization via respiratory  $\text{NH}_3$  when inhaled via the mouth. To the extent that acid deposition to the upper airways is important to subsequent response (e. g., suppressed clearance rate or bronchoconstriction), laryngeal and tracheobronchial deposition is

predicted to be greater when breathing  $\text{H}_2\text{SO}_4$  as fog droplets than as humid haze particles. These fog droplets may also contain additional amounts of labile acids that are not present in significant quantities in humid haze particles. To the extent that alveolar deposition is important to subsequent response, deposition of acid is greater via humid haze particles (RH = 90%) than via fog droplets.

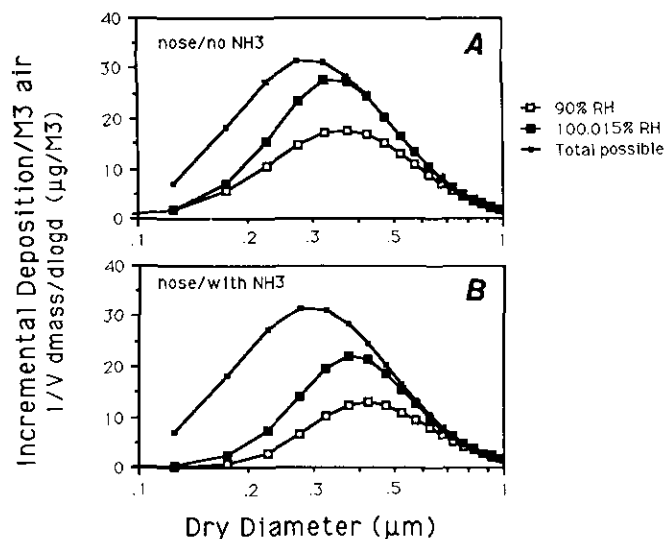


FIGURE 6. Estimated deposition of atmospheric  $\text{H}_2\text{SO}_4$  aerosol/ $\text{m}^3$  air during nose breathing as a function of ambient RH. The calculations were done with and without the presence of respiratory  $\text{NH}_3$  (bottom and top panels, respectively). The ordinate shows the incremental mass deposited/ $\text{m}^3$  dry size interval. "Total possible" represents 100% deposition of the assumed atmospheric size distribution in the absence of  $\text{NH}_3$  neutralization. The area under this curve is therefore the total possible mass of acid deposited per cubic meter of air. The smaller areas under the other curves reflect the fact that less than 100% of all sizes are deposited and (where applicable) that chemical neutralization has occurred prior to deposition.

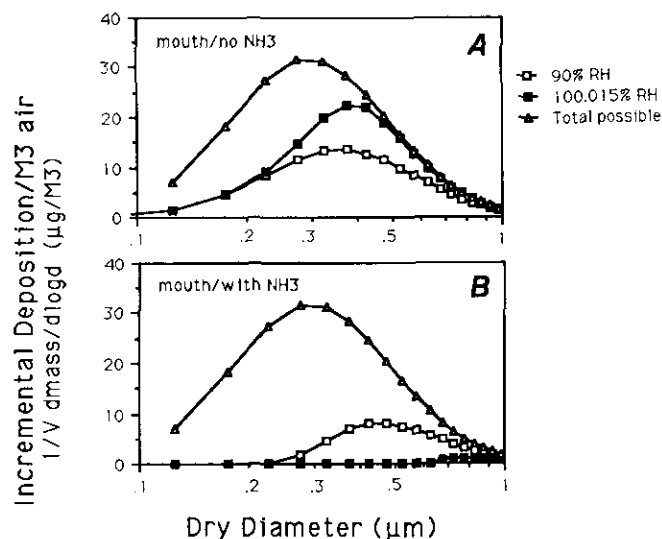


FIGURE 7. Estimated deposition of atmospheric  $\text{H}_2\text{SO}_4$  aerosol/ $\text{m}^3$  of air during mouth breathing as a function of ambient RH. The calculations were done with and without the presence of respiratory  $\text{NH}_3$  (bottom and top panels, respectively). The ordinate shows the incremental mass deposited per cubic meter per dry size interval. "Total possible" represents 100% deposition of the assumed atmospheric size distribution in the absence of  $\text{NH}_3$  neutralization. The area under this curve is therefore the total possible mass of acid deposited per cubic meter of air. The smaller areas under the other curves reflect the fact that less than 100% of all sizes are deposited and (where applicable) that chemical neutralization has occurred prior to deposition.

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